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**DIELECTRIC CURE MONITORING OF THE  
55A FILAMENT WOUND CASE RESIN**

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**ABSTRACT**

Studies have been conducted to correlate data from dielectric cure monitoring of 55A filament wound case resin using the Micromet System II with differential scanning calorimetry and resin strength tests. Strength tests for resin bonding at various time intervals and DSC are standard accepted techniques for monitoring resin cure cycles. They are time consuming, destructive, and non-continuous. The Micromet System II will yield reliable information on degree of cure and other parameters, which should allow better quality control on filament wound case resin cure.

### **Acknowledgements**

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## Introduction

Preliminary studies on dielectric cure monitoring of the Hercules 55A resin have been carried out by Goldberg and Semmel using the Micromet II system developed by Senturia, Day and others. This study continues the work of Goldberg and Semmel with the intention of correlating the dielectric properties of the various resin mixes with data collected from differential scanning calorimetry, bonding strength tests, and solubility considerations. The dielectric parameters of primary concern are loss factor ( $\epsilon''$ ) and permittivity ( $\epsilon'$ ). Loss factor appears to be the more informative property. The permittivity,  $\epsilon'(\omega)$ , is defined as the frequency dependent dielectric constant. The loss factor,  $\epsilon''(\omega)$ , is a measure of the amplitude of the component of the dielectric displacement,  $D(t)$ , 90 degrees out of phase with  $E(t)$ .  $E(t)$  is a cosine term while , the loss factor, is a sine term.

$$D(t) = \epsilon'(\omega) E^0 \cos(\omega t) + \epsilon''(\omega) E^0 \sin(\omega t)$$

$$E(t) = E^0 \cos(\omega t)$$

(Where  $E^0$  is the amplitude of the imposed field and  
 $\omega = 2\pi \text{frequency}$ )

A much more complete description of the Micromet system and explanation of time dependent dielectric measurements may be found in the study by Goldberg and Semmel.

Most of the literature pertinent to microdielectrometry used in the monitoring of epoxy resin cure cycles is found in government contract reports (Ref 2 thru 8). This work resulted in the availability of the Micromet system. The principal advantage of this system is that the transducer is very small and independent of geometric considerations. Dielectric measurements have been made on resins and composite materials for quite some time. There were usually in conjunction with other techniques and with rather cumbersome equipment compared to microdielectrometry. (Ref 9 - 17)

## Procedures

The general procedure for these measurements is to prepare a sample by weighing an amount of resin and catalyst prescribed by specifications. They are mixed thoroughly and divided into aliquots (depending on how many concurrent analyses are to be done). In this work three aliquots are usually sufficient. The aliquot for dielectric analysis is immediately set up and the computer controlled measurement begun. This determination runs continuously for 50 hours with one parameter displayed on the computer screen and data for two parameters plus resin temperature is printed each 15 minutes on a paper roll. All parameters and variables are stored on data tape. An initial DSC (differential scanning calorimetry) determination is made as quickly as possible after starting the micromet run. This involves weighing a small sample, 5 to 20 milligrams, for the DuPont 1090 scanning calorimeter available in the Materials and Processing Laboratory. The initial determination for the heat of reaction is used as the base value for degree of cure. Additional determinations are then obtained as often as possible in keeping with instrument time available and other analyses required. Usually one can do about four to six DSC measurements in an eight hour day. It is desirable to take some data at night while the Micromet run is underway. Once the initial DSC measurement is made the resin mix is prepared for strength tests. This is done by lightly spreading the resin mix on one square inch surface area aluminum blocks. Six samples are prepared with as many replicates as one has blocks. We could do a maximum of two replicates (at least five replicates are needed for statistically significant results). The initial sample is prepared with the original mix, the others require a fresh mix for each sample. The samples are allowed to cure for at least fifty hours and then pulled apart on the Instron instrument and the force recorded. Attempts to do solubility studies by dissolving the resin mix in methyl ethyl ketone and flocking with methyl alcohol were unsuccessful because a satisfactory filtering technique was not found.

## Results and Discussions

This work was confined to the Hercules 55A resin system. Several fifty hour runs were made using the Micromet II microelectrometer system. The runs displayed in this report (Fig 3 - 14) show minimum nominal, and maximum specification resin to catalyst ratios in addition to an excess resin to catalyst run. The figures showing loss factor versus time are overlaid with percent cure and exotherm temperatures from DSC measurements (Fig 3 - 10). There are figures of permittivity versus time for each of the above resin to catalyst ratios. Figure 2 shows a typical DSC run. Table I is compilation of the strength test measurements.

The Micromet II runs of loss factor and permittivity versus time are explained, by Goldberg and Semmel, in terms of gelation and vitrification. Loss factor appears to be the more informative parameter. Several frequencies were monitored, i.e. 100, 500, 1000, 5000, and 10,000 Hz. We have shown only 100, 1000, and 10,000 Hz primarily in the interest of clarity. An explanation for the loss factor curve at 100 Hz (Figures 3 - 10) could be that dipole functions are polymerizing molecules which results in a lower loss factor. The loss factor at 100 Hz declines until about 25 or 30 hours when gelation begins. The loss factor for each frequency then goes through a maximum in this region with the higher frequencies going through the maximum earlier. It is possible that gelation causes the moieties being formed to expend energy in the stiffening medium until solidification stop them from following the changing polarity at all. This earlier maximum for higher frequencies is observed for each resin to catalyst ratio. A general shift of the maxima will occur at different catalyst ratios and temperature. They will occur earlier for higher catalyst concentration and at higher temperatures. The behavior of these maxima at each frequency and the general behavior of the loss factor is a primary reason for the contention that this technique is one of the better ones available for continuous cure monitoring of the 55A resin system. Our work to correlate the system, primarily to DSC measurements, has also tended to support this contention. The dielectric probe is very small, independent of geometry, and nonintrusive, therefore, it is quite possible that in addition to continuous monitoring one could undertake nondestructive spot monitoring of a cure cycle if the proper combination of frequency values for each degree of cure could be determined.

The DSC data for percent cure and exotherm temperature have been overlain on the loss factor plots. Figure 2 shows a typical DSC run is done for each point on the loss factor and permittivity curves. All resin mix cures were done at room temperature for



fifty hours to duplicate the actual situation before oven cure on the filament wound case itself. A small inset on each figure shows a temperature plot for that particular run. Therefore, one can make a mental adjustment for temperature in considering the other variables. The plots for percent cure (Fig. 3, 4, 5, 6) show primarily S-shaped curves indicating that the cure rate tends to increase somewhat until the beginning of gelation and tends to slow after vitrification. This is in agreement with an interpretation of the temperature shift of the exotherm temperature shown in figures 7, 8, 9, and 10. This shift from higher temperatures indicates a lowering of the activation energy until the solidification process. This could be explained as autocatalysis followed by a change in mechanism at vitrification after which the exotherm temperature begins to increase. This type behavior was noted for other similiar epoxy systems being synthesized and studied in this laboratory.

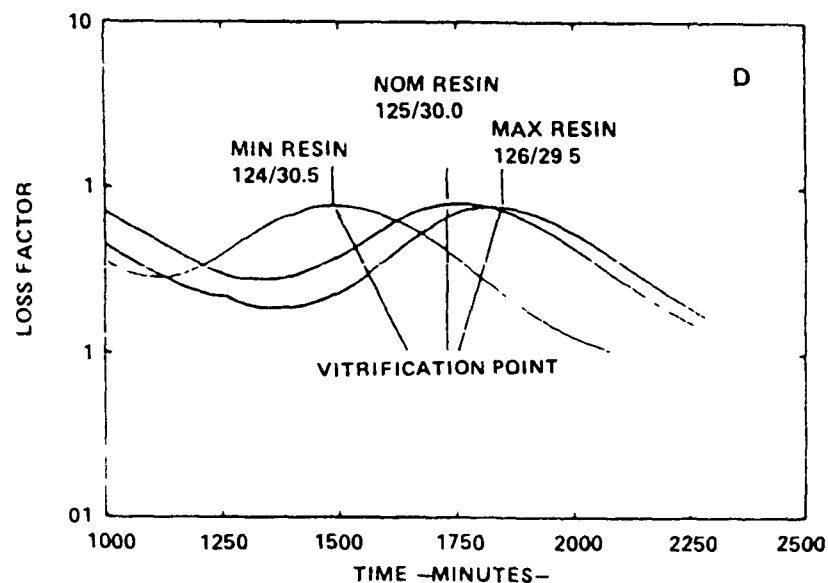
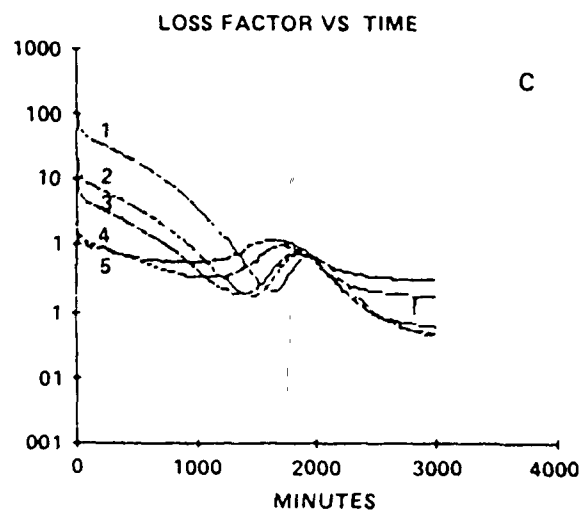
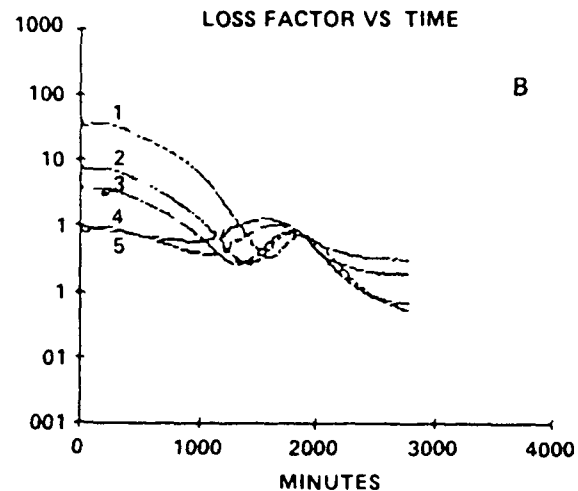
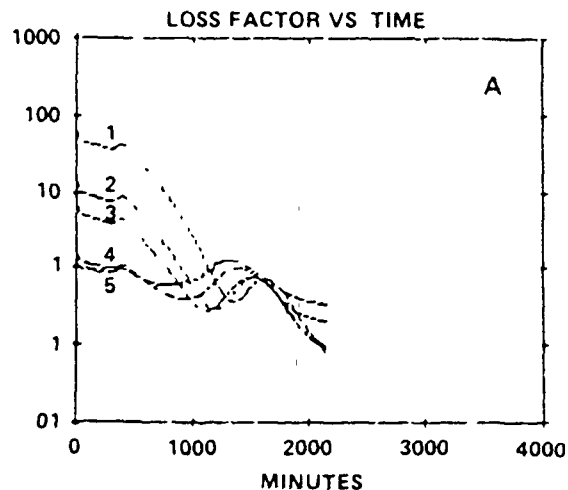
Strength test measurements (Table I), as suggested in the procedural section, required more replicates to be considered good statistical data. However, there are definite trends in bond type and strength. Typically the bonds are cohesive until the beginning of gelation becoming mostly cohesive until vitrification when they become primarily adhesive. The bond strength appears to become generally stronger until vitrification then becoming weaker with more adhesive type bonding, following a rather inverted u-shaped curve from initial mix to fifty hours. A more statistically correct study could be helpful when considering the point at which a mix should be discarded in the event of a breakdown during winding, etc.

### Recommendations

The Micromet II dielectric cure monitoring system should be given serious consideration for the continuous monitoring of the Hercules 55A Filament Wound Case resin. It should be determined if this system could be used as a nondestructive technique for spot monitoring of the resin cure. Arrangements should be made in any further work to take concurrent data at regular intervals throughout the fifty hour cure cycle not just the regular eight hour day period.

**TABLE I**  
**Strength Test Data from 55A Resin Cure Cycles**

<u>Sample</u>	<u>Time (Minutes)</u>	<u>Bond Strength lbs/in<sup>2</sup></u>	<u>Bond Type</u>	<u>Remarks</u>
Nominal Resin 55A-8	Initial	2850	cohesive	
"	379	3450	cohesive	
"	1354	4800	mostly cohesive	
"	1819	4250	cohesive-adhesive	
"	2793	6350	mostly adhesive	anomalous
"	2974	3850	adhesive	
Minimum Resin 55A-10	Initial	1800	cohesive	
"	1118	3600	cohesive	
"	1328	3550	cohesive	
"	1578	3200	mostly cohesive	
"	2623	1600	mostly adhesive	anomalous
"	2958	1900	adhesive	
Maximum Resin 55A-11	Initial	1740	cohesive	
"	1165	3145	cohesive	
"	1505	4480	cohesive	
"	1620	5730	mostly cohesive	
"	1975	2640	adhesive	
"	2935	2535	adhesive	
Excess Resin 55A-7	Initial	1340	cohesive	
"	265	4900	cohesive	
"	1302	4750	cohesive	
"	1688	2840	mostly adhesive	
"	2663	1950	adhesive	
"	2943	—	—	Broken in test



A 124/30.5 RESIN TO CATALYST (BY WEIGHT) RATIO

B 125/30

C 126/29.5

D GEL POINT COMPARISON OF A, B, AND C AT  $\omega = 1$  K Hz.

(1 = 100 Hz, 2 = 500, 3 = 1000 Hz, 4 = 5000 Hz, 5 = 10000 Hz)

FIGURE 1: MICROMET II SCANS OF MINIMUM, NOMINAL, AND MAXIMUM RESIN TO CATALYST RATIOS

Sample: 55A-11RT21.22

Size: 7.84MG

Rate: 20

Program: Interactive DSC V3.0

DSC

Date: 17-Jul-85 Time: 10:53:26

File: 55A.71 LCB DATA CORP3

Operator: RM

Plotted: 17-Jul-85 11:10:54

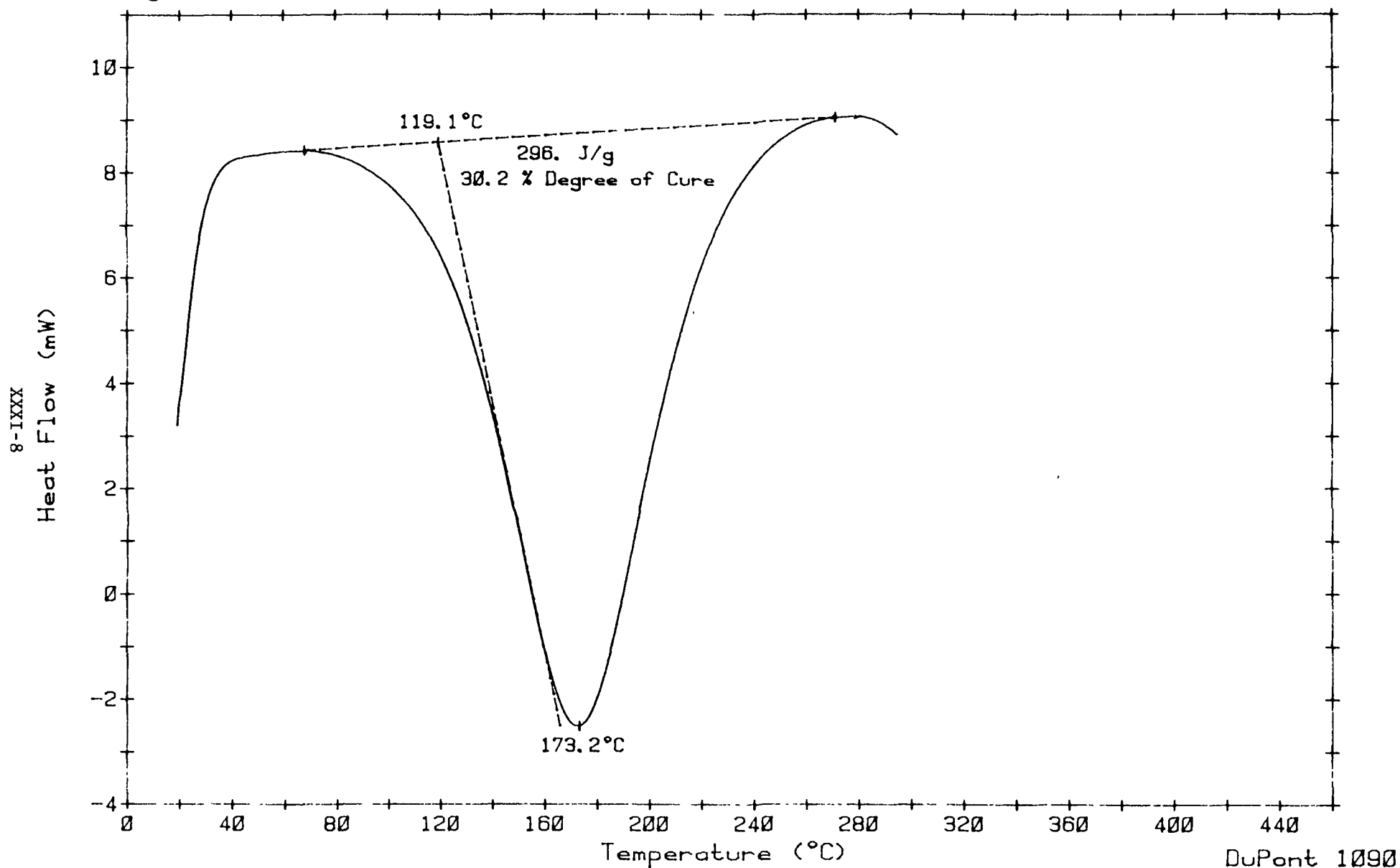


FIGURE 2: TYPICAL DIFFERENTIAL SCANNING CALORIMETER PLOT OF 55A FILAMENT WOUND CASE RESIN DURING CURE CYCLE

6-XXXX

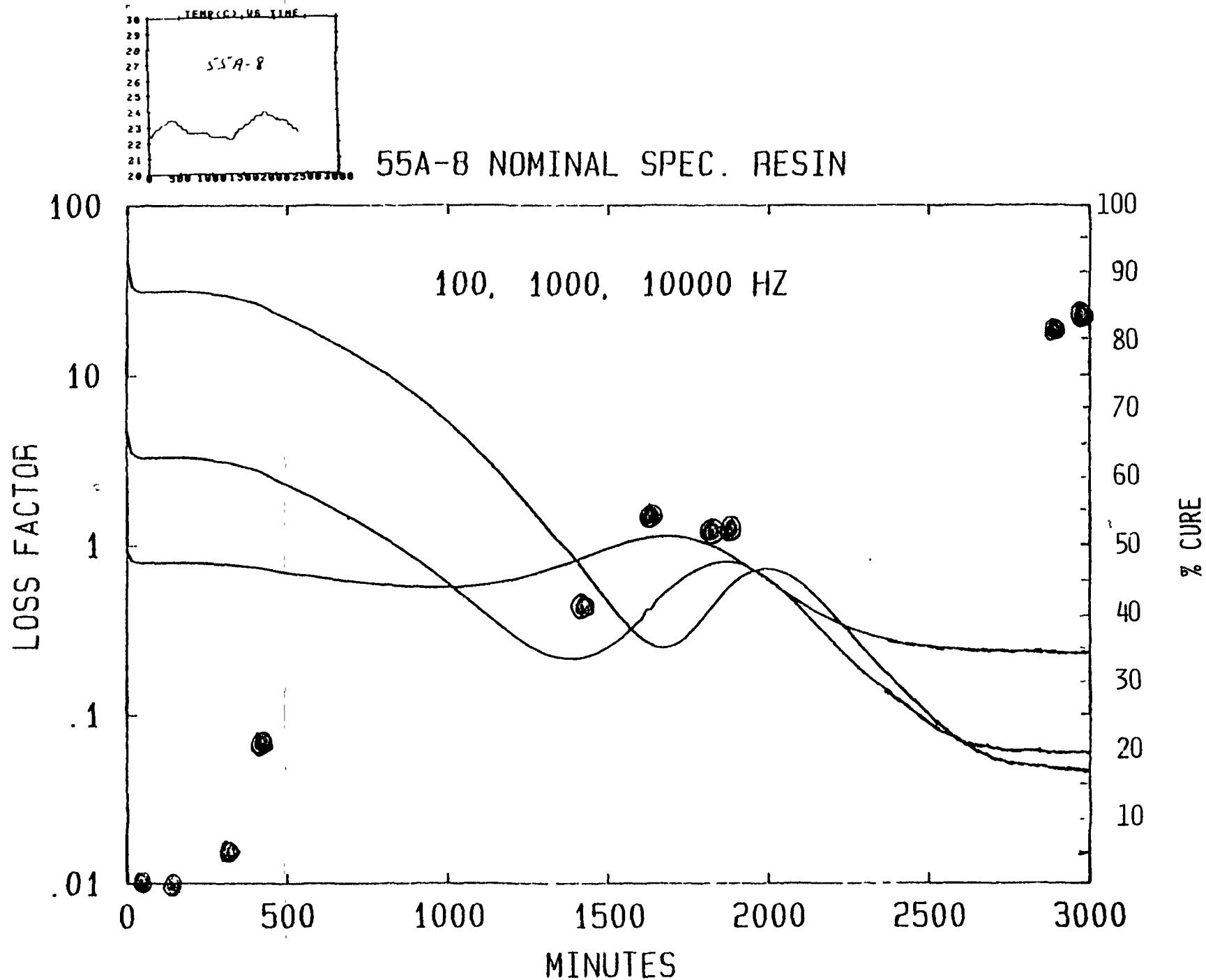


FIGURE 3: LOSS FACTOR VS TIME PLOT OF NOMINAL RESIN TO CATALYST RATIO OVERLAID WITH PERCENT CURE

XXXI-10

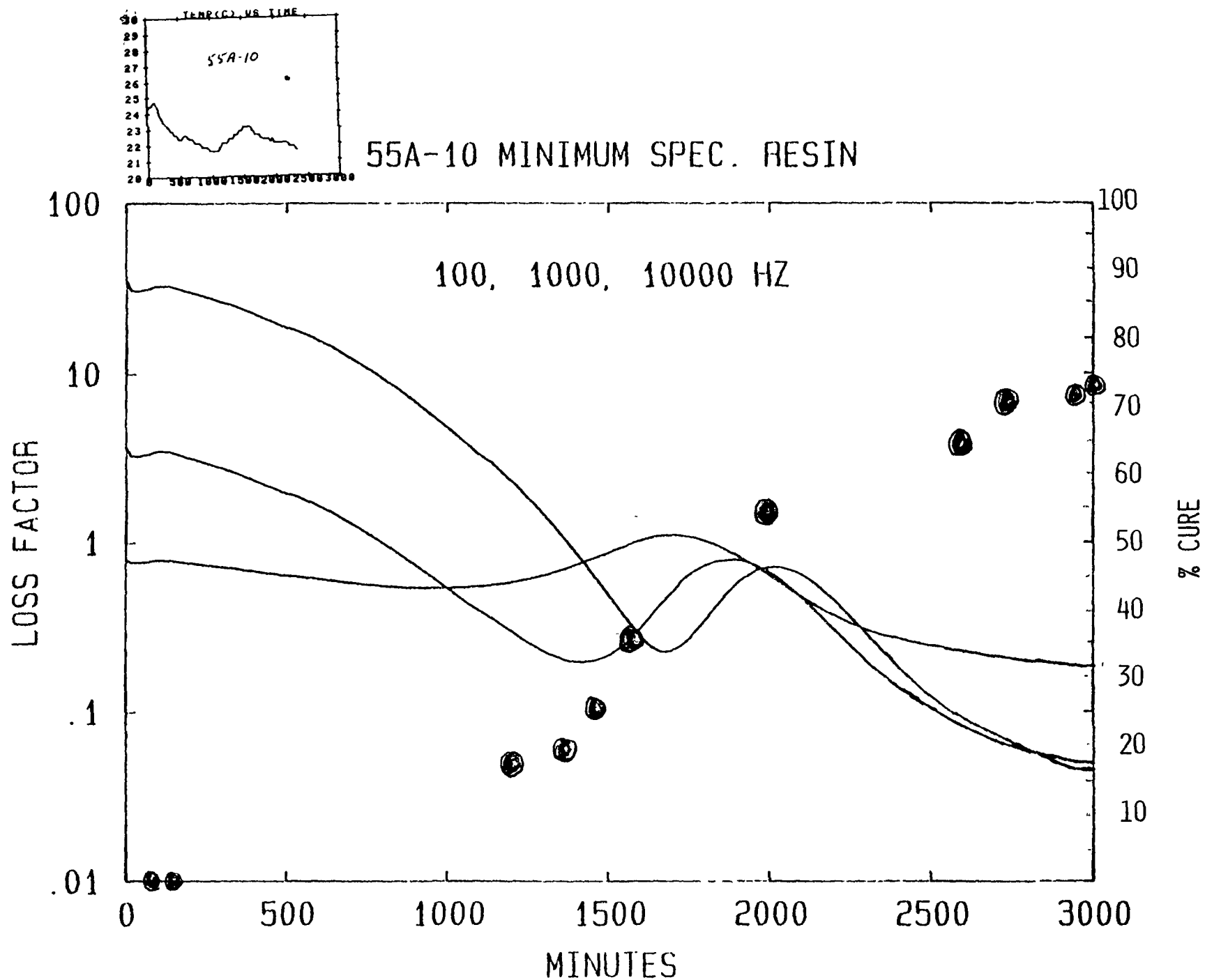


FIGURE 4: Loss Factor vs Time Plot of Minimum Resin to Catalyst Ratio Overlaid With Percent Cure

11-1XXX

b-9

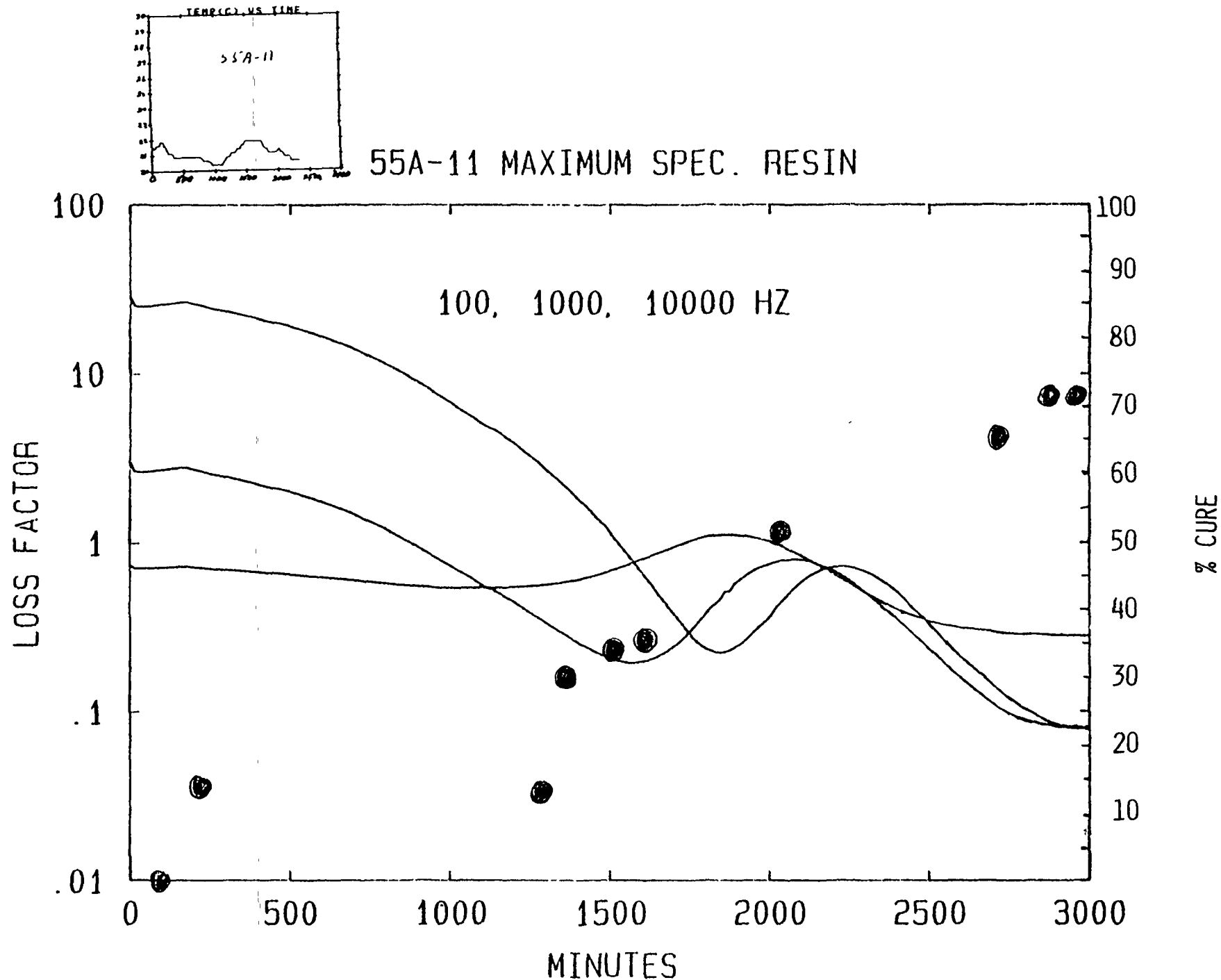


FIGURE 5: LOSS FACTOR VS TIME PLOT OF MAXIMUM RESIN TO CATALYST RATIO OVERLAID WITH PERCENT CURE



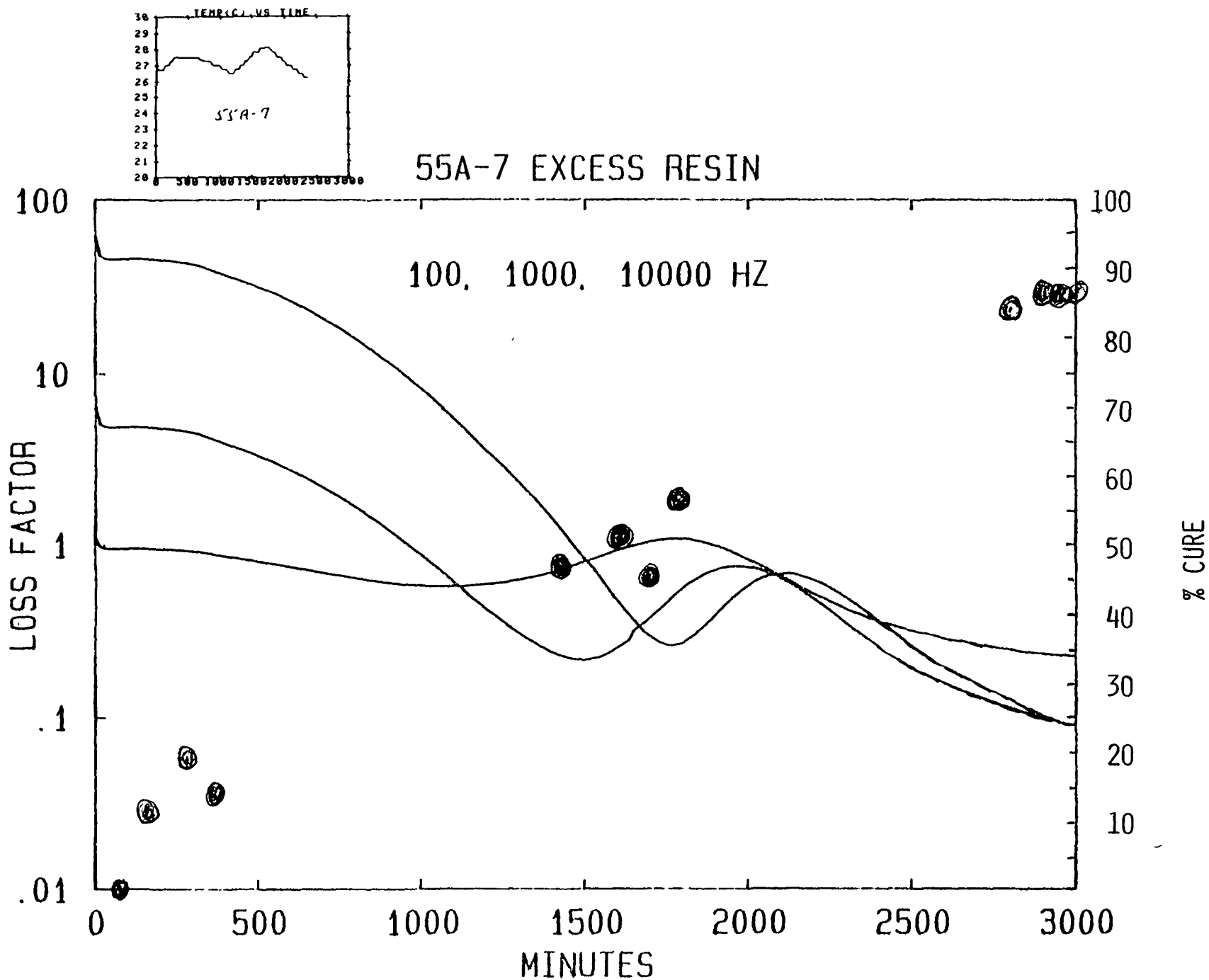


FIGURE 6: LOSS FACTOR VS TIME PLOT OF EXCESS RESIN TO CATALYST RATIO OVERLAID WITH PERCENT CURE

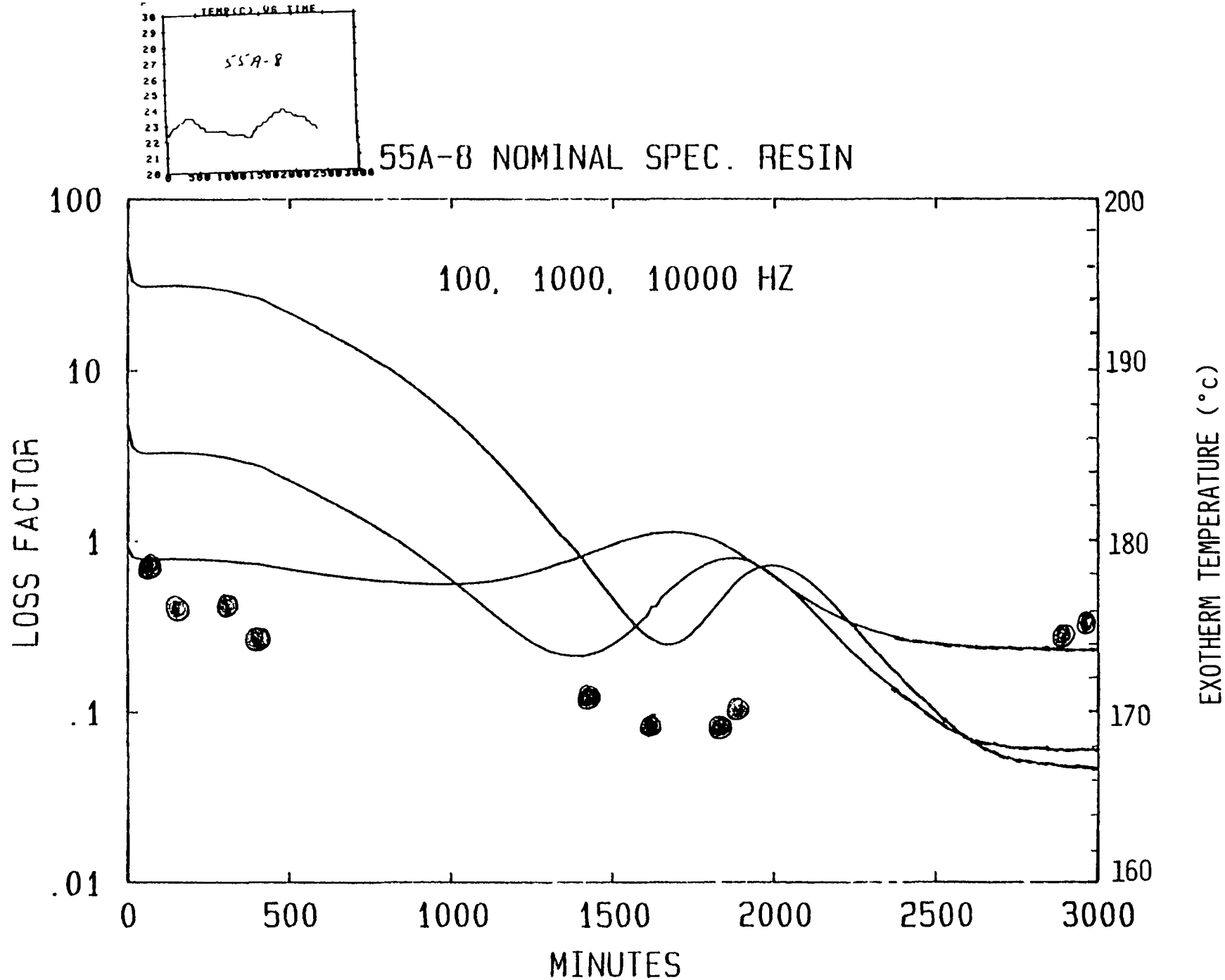


FIGURE 7: LOSS FACTOR VS TIME PLOT OF NOMINAL RESIN TO CATALYST RATIO OVERLAID WITH EXOTHERM TEMPERATURE

41-XXXX

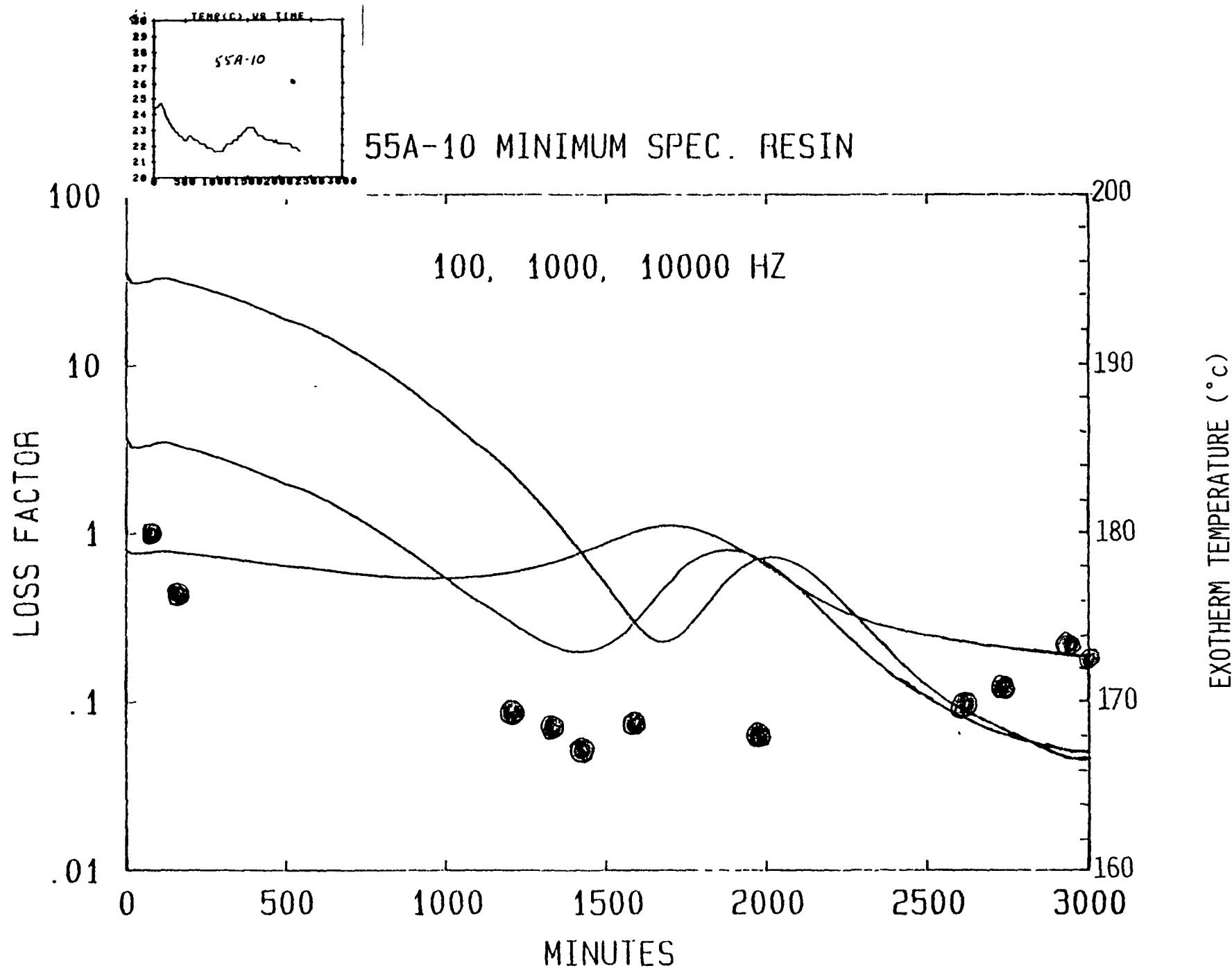


FIGURE 8: LOSS FACTOR VS TIME PLOT OF MINIMUM RESIN TO CATALYST RATIO OVERLAID WITH EXOTHERM TEMPERATURE

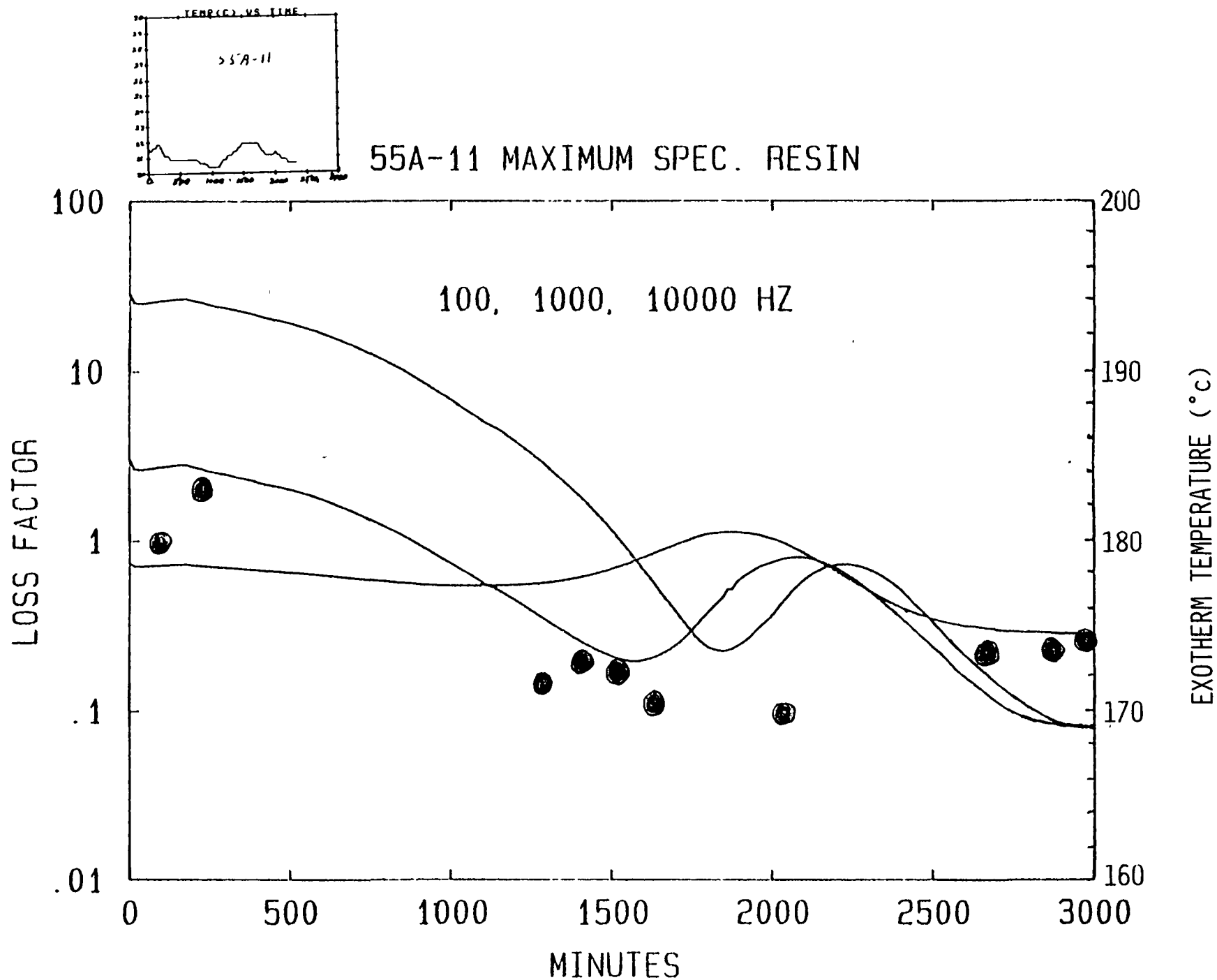


FIGURE 9: LOSS FACTOR VS TIME PLOT OF MAXIMUM RESIN TO CATALYST RATIO OVERLAID WITH EXOTHERM TEMPERATURE

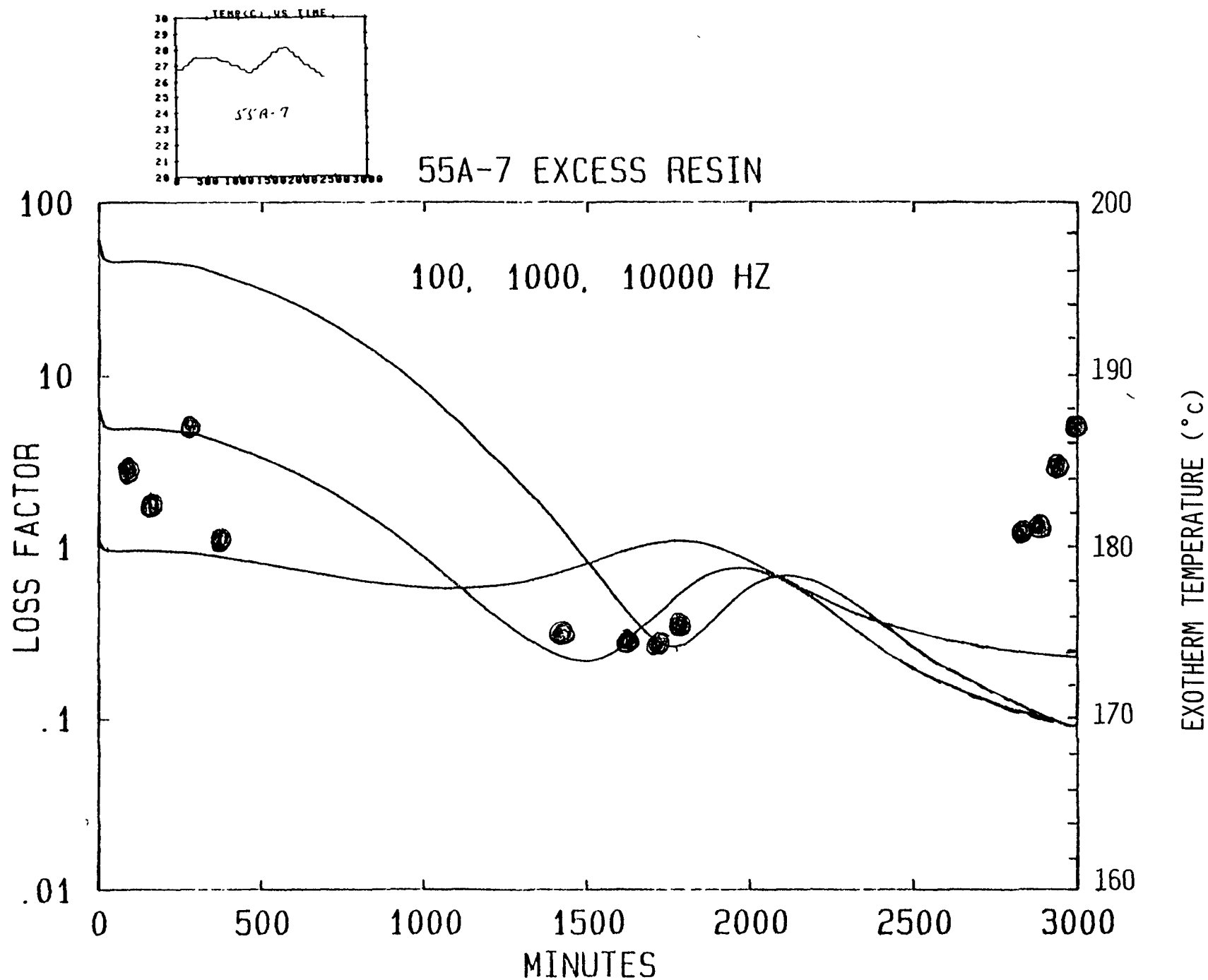


FIGURE 10: LOSS FACTOR VS TIME PLOT OF EXCESS RESIN TO CATALYST RATIO OVERLAID WITH EXOTHERM TEMPERATURE

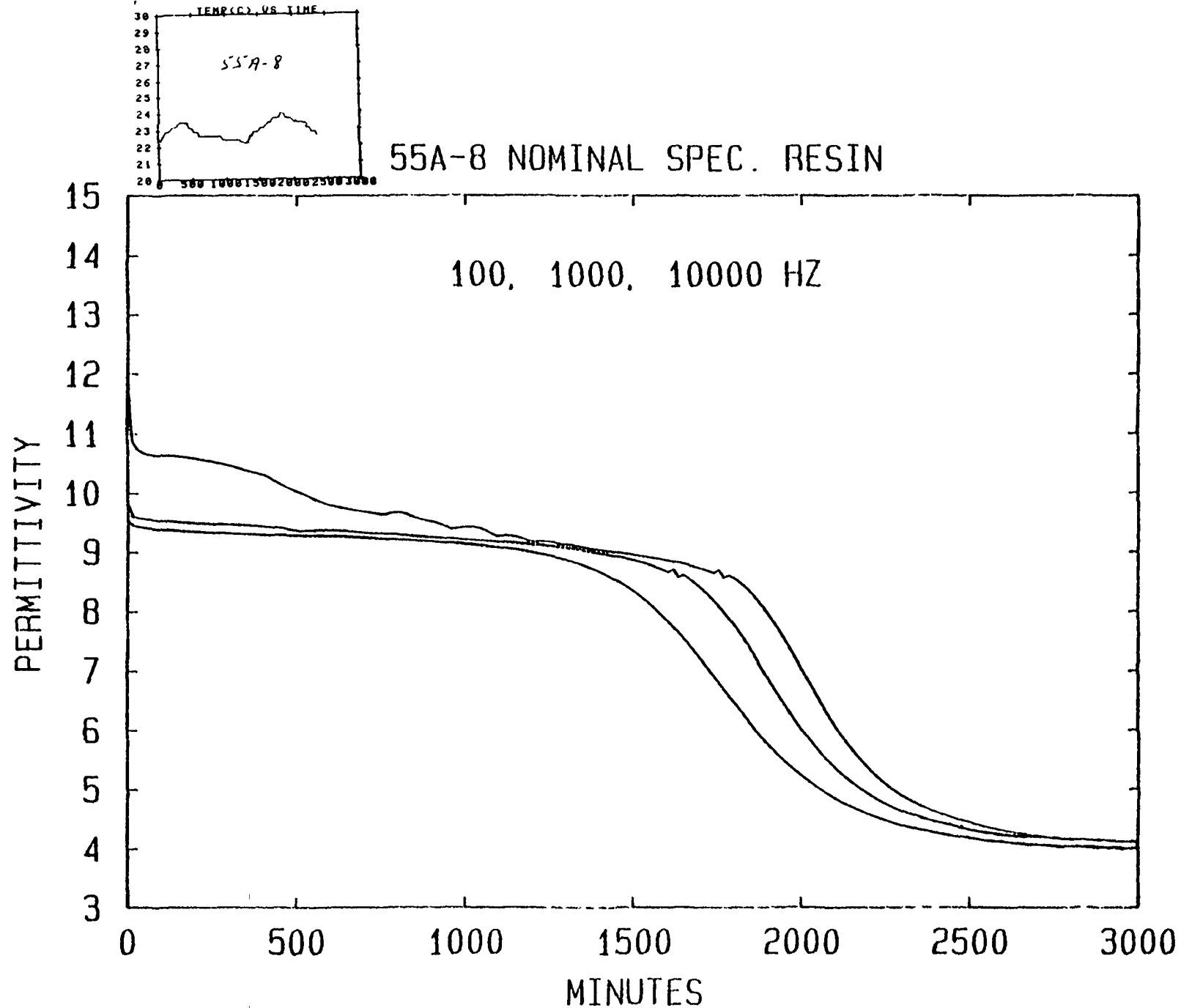


FIGURE 11: PERMITTIVITY VS TIME PLOT OF NOMINAL RESIN TO CATALYST RATIO CURE CYCLE

81-1XXX

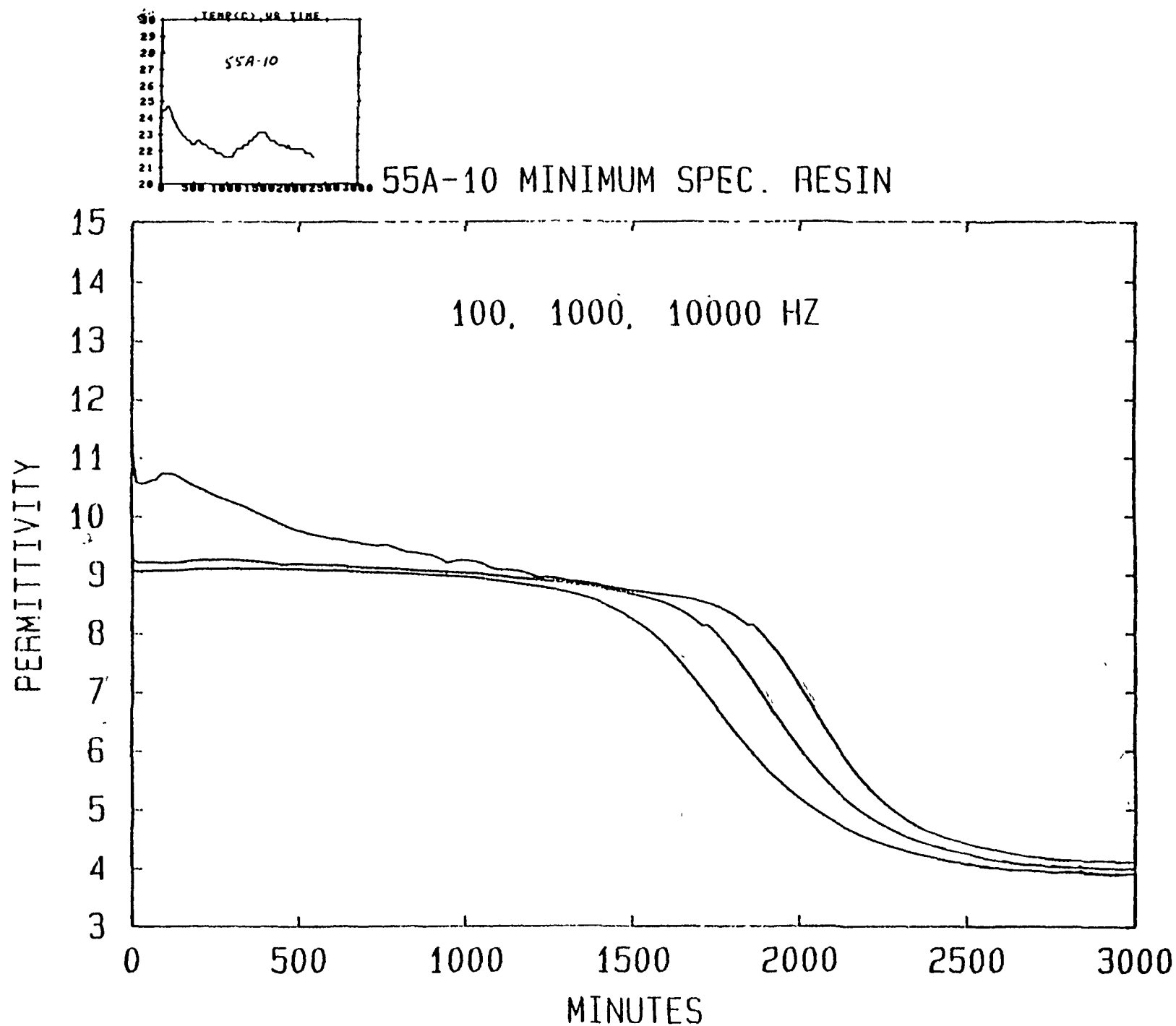


FIGURE 12: PERMITTIVITY VS TIME PLOT OF MINIMUM RESIN TO CATALYST RATIO CURE CYCLE

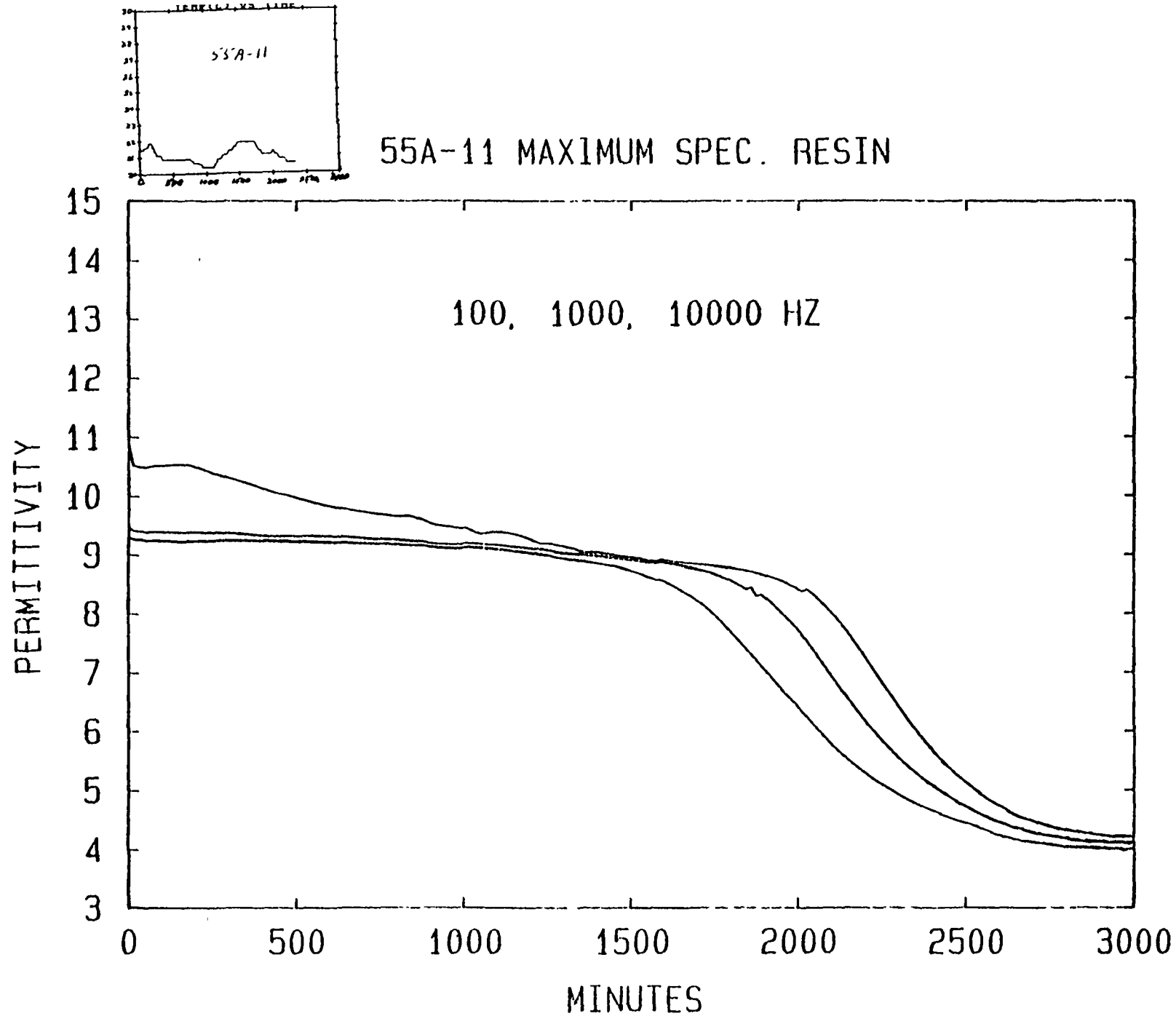


FIGURE 13: PERMITTIVITY VS TIME PLOT OF MAXIMUM RESIN TO CATALYST RATIO CURE CYCLE



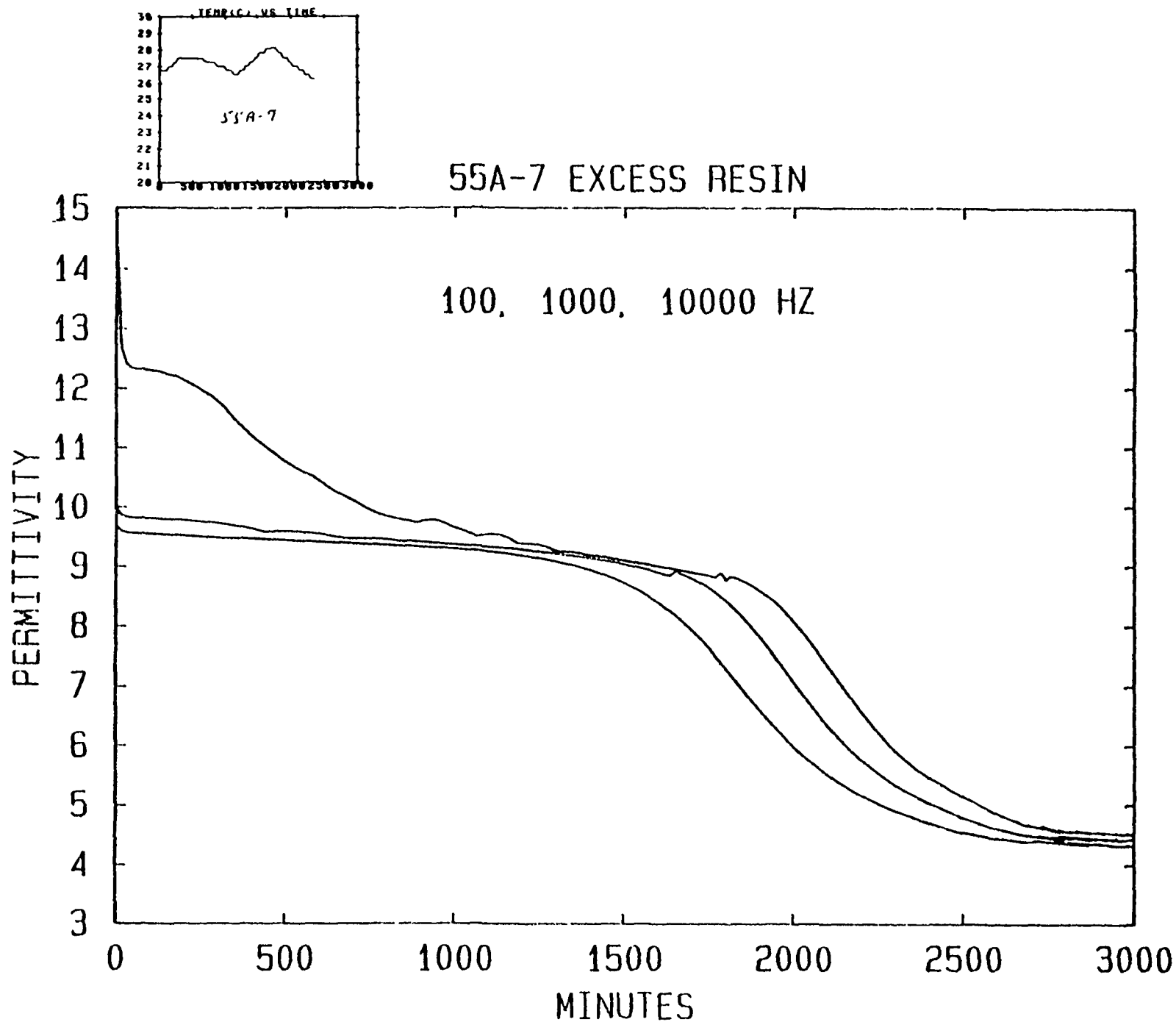


FIGURE 14: PERMITTIVITY VS TIME PLOT OF EXCESS RESIN TO CATALYST RATIO

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